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(PCT Rule 61.2)

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Date of mailing (day/month/year)
17 January 2000 (17.01.00)

International application No.
PCT/SE99/01195

Applicant's or agent's file reference
2991406

International filing date (day/month/year)
01 July 1999 (01.07.99)

Priority date (day/month/year)
06 July 1998 (06.07.98)

Applicant

ASUMALAHTI, Markku et al

1. The designated Office is hereby notified of its election made:

☒ in the demand filed with the International Preliminary Examining Authority on:

26 November 1999 (26.11.99)

☐ in a notice effecting later election filed with the International Bureau on:

2. The election ☒ was

☐ was not

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The International Bureau of WIPO
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1211 Geneva 20, Switzerland

Facsimile No.: (41-22) 740.14.35

Authorized officer

F. Baechler

Telephone No.: (41-22) 338.83.38

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PATENT COOPERATION T. ATY

PCT

NOTIFICATION OF THE RECORDING
OF A CHANGE(PCT Rule 92bis.1 and
Administrative Instructions, Section 422)

From the INTERNATIONAL BUREAU

To:

AWAPATENT AB
P.O. Box 5117
S-200 71 Malmö
SUÈDEDate of mailing (day/month/year)
26 June 2000 (26.06.00)Applicant's or agent's file reference
2991406

IMPORTANT NOTIFICATION

International application No.
PCT/SE99/01195International filing date (day/month/year)
01 July 1999 (01.07.99)

1. The following indications appeared on record concerning:

☒ the applicant ☐ the inventor ☐ the agent ☐ the common representative

Name and Address

BOREALIS POLYMERS OY
P.O. Box 330
FIN-06101 Porvoo
Finland

State of Nationality

FI

State of Residence

FI

Telephone No.

Facsimile No.

Teleprinter No.

2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:

☒ the person ☒ the name ☐ the address ☐ the nationality ☐ the residence

Name and Address

BOREALIS TECHNOLOGY OY
P.O. Box 330
FIN-06101 Porvoo
Finland

State of Nationality

FI

State of Residence

FI

Telephone No.

Facsimile No.

Teleprinter No.

3. Further observations, if necessary:

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☐ the International Searching Authority ☒ the elected Offices concerned
☒ the International Preliminary Examining Authority ☐ other:The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Authorized officer

Beate Giffo-Schmitt

Facsimile No.: (41-22) 740.14.35

Telephone No.: (41-22) 338.83.38

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PATENT COOPERATION T. ATY

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From the INTERNATIONAL BUREAU

NOTIFICATION OF THE RECORDING
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To:

AWAPATENT AB
P.O. Box 5117
S-200 71 Malmö
SUÈDE

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International application No. PCT/SE99/01195	International filing date (day/month/year) 01 July 1999 (01.07.99)

1. The following indications appeared on record concerning:		
<input checked="" type="checkbox"/> the applicant	<input type="checkbox"/> the inventor	<input type="checkbox"/> the agent <input type="checkbox"/> the common representative
Name and Address BOREALIS POLYMERS OY P.O. Box 330 FIN-06101 Porvoo Finland	State of Nationality FI	State of Residence FI
	Telephone No.	
	Facsimile No.	
	Teleprinter No.	
2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:		
<input checked="" type="checkbox"/> the person	<input checked="" type="checkbox"/> the name	<input type="checkbox"/> the address <input type="checkbox"/> the nationality <input type="checkbox"/> the residence
Name and Address BOREALIS TECHNOLOGY OY P.O. Box 330 FIN-06101 Porvoo Finland	State of Nationality FI	State of Residence FI
	Telephone No.	
	Facsimile No.	
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The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland	Authorized officer Beate Giffo-Schmitt
Facsimile No.: (41-22) 740.14.35	Telephone No.: (41-22) 338.83.38

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PATENT COOPERATION TREATY

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NOTIFICATION OF THE RECORDING
OF A CHANGE(PCT Rule 92bis.1 and
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From the INTERNATIONAL BUREAU

To:

AWAPATENT AB
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1. The following indications appeared on record concerning:

☒ the applicant ☒ the inventor ☐ the agent ☐ the common representative

Name and Address PALMROOS, Ari Haltijakuja 4F 19 FIN-04230 Kerava Finland	State of Nationality FI	State of Residence FI
	Telephone No.	
	Facsimile No.	
	Teleprinter No.	

2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:

☐ the person ☐ the name ☒ the address ☐ the nationality ☐ the residence

Name and Address PALMROOS, Ari Annantie 11 FIN-06400 Porvoo Finland	State of Nationality FI	State of Residence FI
	Telephone No.	
	Facsimile No.	
	Teleprinter No.	

3. Further observations, if necessary:

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The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland	Authorized officer: Marie-José Devillard
Facsimile No.: (41-22) 740.14.35	Telephone No.: (41-22) 338.83.38

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<p>(21) International Application Number: PCT/SE99/01195</p> <p>(22) International Filing Date: 1 July 1999 (01.07.99)</p> <p>(30) Priority Data: 9802409-4 6 July 1998 (06.07.98) SE</p> <p>(71) Applicant (for all designated States except US): BOREALIS POLYMERS OY [FI/FI]; P.O. Box 330, FIN-06101 Porvoo (FI).</p> <p>(72) Inventors; and (75) Inventors/Applicants (for US only): ASUMALAHTI, Markku [FI/FI]; Louhenkuja 3, FIN-04230 Kerava (FI). ÄÄRILÄÄ, Jari [FI/FI]; Partiomiehentie 1B 31, FIN-06100 Porvoo (FI). PALMROOS, Ari [FI/FI]; Haltijakuja 4F 19, FIN-04230 Kerava (FI). BÄCKMAN, Mats [SE/SE]; Forsstenagatan 4 H, S-416 51 Göteborg (SE). NILSSON, Anette [SE/SE]; Hermans väg 11, S-444 60 Stora Höga (SE). PALMLÖF, Magnus [SE/SE]; Nya Varvet 9, S-426 71 Västra Frölunda (SE).</p> <p>(74) Agent: AWAPATENT AB; P.O. Box 5117, S-200 71 Malmö (SE).</p>	<p>(81) Designated States: AE, AL, AM, AT, AT (Utility model), AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, CZ (Utility model), DE, DE (Utility model), DK, DK (Utility model), EE, EE (Utility model), ES, FI, FI (Utility model), GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (Utility model), SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</p> <p>Published With international search report.</p>	
<p>(54) Title: POLYMER COMPOSITION FOR PIPES</p>		
<p>(57) Abstract</p> <p>A multimodal polymer composition for pipes is disclosed. The polymer is a multimodal polyethylene with a density of 0.930–0.965 g/cm³, an MFR₅ of 0.2–1.2 g/10 min, and M_n of 8000–15000, an M_w of 180–330 x 10³, and an M_w/M_n of 20–35, said multimodal polyethylene comprising a low molecular weight (LMW) ethylene homopolymer fraction and a high molecular weight (HMW) ethylene copolymer fraction, said HMW fraction having a lower molecular weight limit of 3500, and a weight ratio of the LMW fraction to the HMW fraction of (35–55) : (65–45).</p>		

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POLYMER COMPOSITION FOR PIPESField of the invention

The present invention relates to a multimodal polymer composition for pipes and a pipe prepared thereof.

Background of the invention

5 Nowadays, pipes of polymer material are frequently used for various purposes, such as fluid transport, i.e. transport of liquid or gas, e.g. water or natural gas, during which the fluid can be pressurised. Moreover, the transported fluid may have varying temperatures, usually
10 within the temperature range from about 0°C to about 50°C. Such pressure pipes are preferably made of polyolefin plastic, usually unimodal ethylene plastic such as medium density polyethylene (MDPE; density: 0.930-0.942 g/cm³) and high density polyethylene (HDPE; density: 0.945-
15 -0.965 g/cm³). By the expression "pressure pipe" herein is meant a pipe which, when used, is subjected to a positive pressure, i.e. the pressure inside the pipe is higher than the pressure outside the pipe.

 Polymer pipes are generally manufactured by extrusion, or, to a smaller extent, by injection moulding. A
20 conventional plant for extrusion of polymer pipes comprises an extruder, a nozzle, a calibrating device, cooling equipment, a pulling device, and a device for cutting or for coiling-up the pipe.

25 The properties of such conventional polymer pipes are sufficient for many purposes, although enhanced
~~properties may be desired, for instance in applications~~
 requiring high pressure resistance, i.e. pipes that are subjected to an internal fluid pressure for a long and/or
30 short period of time. As examples of properties which it is desirable to improve may be mentioned the processability, the impact strength, the modulus of elasticity, the
~~rapid crack propagation resistance, the slow crack growth resistance, and the design stress rating of the pipe.~~

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Summary of the invention

It has now been discovered that a superior pressure pipe may be obtained by preparing it from a specific, well defined type of multimodal polyethylene. More particularly, the multimodal polyethylene should have a medium to high density, have a broad molecular weight distribution, a carefully selected ratio between its low molecular weight fraction and high molecular weight fraction, and include a comonomer in its high molecular weight fraction only.

Thus, the present invention provides a multimodal polyethylene composition for pipes, which multimodal polyethylene has a density of 0.930-0.965 g/cm³ and an MFR₅ of 0.2-1.2 g/10 min, characterised in that the multimodal polyethylene has an M_n of 8000-15000, an M_w of 180-330 x 10³, and an M_w/M_n of 20-35, said multimodal polyethylene comprising a low molecular weight (LMW) ethylene homopolymer fraction and a high molecular weight (HMW) ethylene copolymer fraction, said HMW fraction having a lower molecular weight limit of 3500, and a weight ratio of the LMW fraction to the HMW fraction of (35-55):(65-45).

Other distinguishing features and advantages of the invention will appear from the following specification and the appended claims.

Detailed description of the invention

As stated above, the pressure pipe composition of the present invention is made from a multimodal polyethylene. This is in contrast to prior art polyethylene pipes which usually are made of unimodal polyethylene.

The "modality" of a polymer refers to the form of its molecular weight distribution curve, i.e. the appearance of the graph of the polymer weight fraction as function of its molecular weight. If the polymer is produced in a sequential step process, utilizing reactors coupled in series and using different conditions in each reactor, the different fractions produced in the different reactors

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will each have their own molecular weight distribution. When the molecular weight distribution curves from these fractions are superimposed into the molecular weight distribution curve for the total resulting polymer product, that curve will show two or more maxima or at least be distinctly broadened in comparison with the curves for the individual fractions. Such a polymer product, produced in two or more serial steps, is called bimodal or multimodal depending on the number of steps. In the following all polymers thus produced in two or more sequential steps are called "multimodal". It is to be noted here that also the chemical compositions of the different fractions may be different. Thus one or more fractions may consist of an ethylene copolymer, while one or more others may consist of ethylene homopolymer.

By properly selecting the different polymer fractions and the proportions thereof in the multimodal polyethylene a pipe with inter alia enhanced processability can be obtained.

The pressure pipe composition of the present invention is a multimodal polyethylene, preferably a bimodal polyethylene. The multimodal polyethylene comprises a low molecular weight (LMW) ethylene homopolymer fraction and a high molecular weight (HMW) ethylene copolymer fraction. Depending on whether the multimodal polyethylene is bimodal or has a higher modality the LMW and HMW fractions may comprise only one fraction each or include sub-fractions, i.e. the LMW may comprise two or more LMW sub-fractions and similarly the HMW fraction may comprise two or more HMW sub-fractions. It is a characterising feature of the present invention that the LMW fraction is an ethylene homopolymer and that the HMW fraction is an ethylene copolymer, i.e. it is only the HMW fraction that includes a comonomer. As a matter of definition, the expression "ethylene homopolymer" used herein relates to an ethylene polymer that consists substantially, i.e. to at least 97% by weight, preferably at least 99% by

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weight, more preferably at least 99.5% by weight, and most preferably at least 99.8% by weight of ethylene and thus is an HD ethylene polymer which preferably only includes ethylene monomer units. Moreover, the lower
5 limit of the molecular weight range of the HMW fraction is 3 500, preferably 4000. This means that almost all ethylene copolymer molecules in the multimodal polyethylene pipe composition of the invention have a molecular weight of at least 3500, preferably at least 4000.
10 The reason for this is that the presence of comonomer in the LMW fraction gives a pressure pipe with poor strength.

In the present invention it is further important that the proportions of the LMW and HMW fractions (also
15 known as the "split" between the fractions) are selected properly. More particularly, the weight ratio of the LMW fraction to the HMW fraction should lie in the range (35-55):(65-45), preferably (43-51):(57-49), most preferably (43-48):(57-52). It is important that the split
20 lies within these ranges, because if the proportion of the HMW fraction becomes too great it results in too low strength values and if it is too low it results in an unacceptable formation of gels.

The molecular weight distribution, as defined by the
25 ratio of the weight average molecular weight (M_w) to the number average molecular weight (M_n), i.e. M_w/M_n , of the multimodal polyethylene is rather broad at the present invention and has a value of 20-35, preferably 22-30. The reason for this is to obtain a pressure pipe with a desired combination of good processability and good
30 strength. Further, the number average molecular weight, M_n , has a value of 8 000-15 000, preferably 9 000-14 000, while the weight average molecular weight, M_w , has a value of ~~180-330~~ $\times 10^3$, preferably ~~200-320~~ $\times 10^3$
35 (180-260 $\times 10^3$, preferably 200-250 $\times 10^3$, for an MD pipe material and 250-330 $\times 10^3$, preferably 280-320 $\times 10^3$, for an HD pipe material).

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The melt flow rate (MFR), which is equivalent to the term "melt index" previously used, is another important property of the multimodal polyethylene for pipes according to the invention. The MFR is determined according to ISO 1133 and is indicated in g/10 min. The MFR is an indication of the flowability, and hence the processability, of the polymer. The higher the melt flow rate, the lower the viscosity of the polymer. The MFR is determined at different loadings such as 2.1 kg (MFR_{2.1}; ISO 1133, condition D) or 5 kg (MFR₅; ISO 1133, condition T). At the present invention the multimodal polyethylene has an MFR₅ of 0.2-1.2 g/10 min, preferably 0.3-1.0 g/10 min.

Another characterising feature of the present invention is the density of the multimodal polyethylene. For reasons of strength the density lies in the medium to high density range, more particularly in the range 0.930-0.965 g/cm³. Preferably, lower densities of 0.937-0.942 g/cm³ are used for smaller diameter MD pressure pipes, while higher densities of 0.943-0.955 g/cm³ are used for larger diameter HD pressure pipes. The pressure pipes of medium density multimodal polyethylene are somewhat more flexible than pressure pipes of high density multimodal polyethylene and may therefore more easily be coiled into a roll. On the other hand it is possible to obtain pressure pipes of a higher design stress rating with high density multimodal polyethylene than with medium density multimodal polyethylene.

It should be noted that the multimodal polymer composition of the present invention is characterised, not by any single one of the above defined features, but by the combination of all the features defined in claim 1. By this unique combination of features it is possible to obtain pressure pipes of superior performance, particularly with regard to processability, rapid crack propagation (RCP) resistance, design stress rating, impact strength, and slow crack growth resistance.

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The processability of a pipe (or rather the polymer thereof) may be determined in terms of the number of screw revolutions per minute (rpm) of an extruder for a predetermined output of pipe in kg/h, but also the surface appearance of the pipe is then important.

The rapid crack propagation (RCP) resistance of a pipe may be determined according to a method called the S4 test (Small Scale Steady State), which has been developed at Imperial College, London, and which is described in ISO DIS 13477. According to the RCP-S4 test a pipe is tested, which has an axial length not below 7 pipe diameters. The outer diameter of the pipe is about 110 mm or greater and its wall thickness about 10 mm or greater. When determining the RCP properties of a pipe in connection with the present invention, the outer diameter and the wall thickness have been selected to be 110 mm and 10 mm, respectively. While the exterior of the pipe is at ambient pressure (atmospheric pressure), the pipe is pressurised internally, and the internal pressure in the pipe is kept constant at a pressure of 0.5 MPa positive pressure. The pipe and the equipment surrounding it are thermostatted to a predetermined temperature. A number of discs have been mounted on a shaft inside the pipe to prevent decompression during the tests. A knife projectile is shot, with well-defined forms, towards the pipe close to its one end in the so-called initiating zone in order to start a rapidly running axial crack. The initiating zone is provided with an abutment for avoiding unnecessary deformation of the pipe. The test equipment is adjusted in such a manner that crack initiation takes place in the material involved, and a number of tests are effected at varying temperatures. The axial crack length in the measuring zone, having a total length of 4.5 diameters, is measured for each test and is plotted against the set test temperature. If the crack length exceeds 4 diameters, the crack is assessed to propagate. If the pipe passes the test at a given temperature, the temperature is lowered

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successively until a temperature is reached, at which the pipe no longer passes the test, but the crack propagation exceeds 4 times the pipe diameter. The critical temperature (T_{crit}) i.e. the ductile brittle transition temperature as measured according to ISO DIS 13477 is the lowest temperature at which the pipe passes the test. The lower the critical temperature the better, since it results in an extension of the applicability of the pipe. It is desirable for the critical temperature to be around -5°C or lower. A pressure pipe made of the multimodal polymer composition according to the present invention preferably has an RCP-S4 value of -1°C (minimum requirement for an MD PE80 pipe) or lower, more preferably -4°C (minimum requirement for an HD PE80 pipe) or lower, and most preferably -7°C (minimum requirement for an HD PE100 pipe) or lower.

The design stress rating is the circumferential stress a pipe is designed to withstand for 50 years without failure and is determined for different temperatures in terms of the Minimum Required Strength (MRS) according to ISO/TR 9080. Thus, MRS8.0 means that the pipe is a pipe withstanding an internal pressure of 8.0 MPa gauge for 50 years at 20°C , and similarly MRS10.0 means that the pipe withstands an internal pressure of 10 MPa gauge for 50 years at 20°C . A pressure pipe made of the multimodal polymer composition according to the present invention preferably has a design stress rating of at least MRS8.0, and most preferably MRS10.0.

The impact strength is determined as Charpy Impact Strength according to ISO 179. ~~A pressure pipe made of the multimodal polymer composition according to the present invention preferably has an impact resistance at 0°C of at least 10 kJ/m^2 , more preferably at least 14 kJ/m^2 , and most preferably at least 15 kJ/m^2 .~~

The slow crack propagation resistance is determined according to ISO 13479:1997 in terms of the number of hours the pipe withstands a certain pressure at a certain

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temperature before failure. A pressure pipe made of the multimodal polymer composition according to the present invention preferably has a slow crack propagation resistance of at least 1000 hrs at 4.0 MPa/80°C, and more preferably at least 500 hrs at 4.6 MPa/80°C.

The modulus of elasticity is determined according to ISO 527-2/1B. A pressure pipe made of the multimodal polymer composition according to the present invention preferably has a modulus of elasticity of at least 800 MPa, more preferably at least 950 MPa, and most preferably at least 1100 MPa.

A pressure pipe made of the multimodal polymer composition of the present invention is prepared in a conventional manner, preferably by extrusion in an extruder. This is a technique well known to the skilled person and no further particulars should therefore be necessary here concerning this aspect.

It is previously known to produce multimodal, in particular bimodal, olefin polymers, such as multimodal polyethylene, in two or more reactors connected in series. As an instance of this prior art, mention may be made of EP 517 868, which is hereby incorporated by way of reference as regards the production of multimodal polymers.

According to the present invention, the main polymerisation stages are preferably carried out as a combination of slurry polymerisation/gas-phase polymerisation. The slurry polymerisation is preferably performed in a so-called loop reactor. The use of slurry polymerisation in a stirred-tank reactor is not preferred in the present invention, since such a method is not sufficiently flexible for the production of the inventive composition and involves solubility problems. In order to produce the inventive composition of improved properties, a flexible method is required. For this reason, it is preferred that the composition is produced in two main polymerisation stages in a combination of loop reactor/gas-phase reactor. Optionally and advantageously, the main polymerisation

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stages may be preceded by a prepolymerisation, in which case up to 20% by weight, preferably 1-10% by weight, more preferably 1-5% by weight, of the total amount of polymers is produced. The prepolymer is preferably an ethylene homopolymer (HDPE). At the prepolymerisation all of the catalyst is preferably charged into a loop reactor and the prepolymerisation is performed as a slurry polymerisation. Such a prepolymerisation leads to less fine particles being produced in the following reactors and to a more homogeneous product being obtained in the end. Generally, this technique results in a multimodal polymer mixture through polymerisation with the aid of a Ziegler-Natta or metallocene catalyst in several successive polymerisation reactors. Chromium catalysts are not preferred in connection with the present invention because of the high degree of unsaturation they confer to the polymer. In the production of, say, a bimodal polyethylene, which according to the invention is the preferred polymer, a first ethylene polymer is produced in a first reactor under certain conditions with respect to hydrogen-gas pressure, temperature, pressure, and so forth. After the polymerisation in the first reactor, the reaction mixture including the polymer produced is fed to a second reactor, where further polymerisation takes place under other conditions. Usually, a first polymer of high melt flow rate (low molecular weight, LMW) and with no addition of comonomer is produced in the first reactor, whereas a second polymer of low melt flow rate (high molecular weight, HMW) and with addition of comonomer is produced in the second reactor. As comonomer of the HMW fraction various ~~alpha-~~olefins with 4-8 carbon atoms may be used, but the comonomer is preferably selected from the group consisting of 1-butene, 1-hexene, 4-methyl-1-pentene, and 1-octene. ~~The amount of comonomer is preferably such that it~~ comprises 0.4-3.5 mol%, more preferably 0.7-2.5 mol% of the multimodal polyethylene. The resulting end product consists of an intimate mixture of the polymers from the

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two reactors, the different molecular-weight-distribution curves of these polymers together forming a molecular-weight-distribution curve having a broad maximum or two maxima, i.e. the end product is a bimodal polymer mixture.

5 Since multimodal, and especially bimodal, ethylene polymers, and the production thereof belong to the prior art, no detailed description is called for here, but reference is had to the above mentioned EP 517 868.

As hinted above, it is preferred that the multimodal
10 polyethylene composition according to the invention is a bimodal polymer mixture. It is also preferred that this bimodal polymer mixture has been produced by polymerisation as above under different polymerisation conditions in two or more polymerisation reactors connected in
15 series. Owing to the flexibility with respect to reaction conditions thus obtained, it is most preferred that the polymerisation is carried out in a loop reactor/a gas-phase reactor. Preferably, the polymerisation conditions in the preferred two-stage method are so chosen
20 that a comparatively low-molecular polymer having no content of comonomer is produced in one stage, preferably the first stage, owing to a high content of chain-transfer agent (hydrogen gas), whereas a high-molecular polymer having a content of comonomer is produced in another
25 stage, preferably the second stage. The order of these stages may, however, be reversed.

In the preferred embodiment of the polymerisation in a loop reactor followed by a gas-phase reactor, the polymerisation temperature in the loop reactor preferably is
30 92-98°C, more preferably about 95°C, and the temperature in the gas-phase reactor preferably is 75-90°C, more preferably 80-85°C.

A chain-transfer agent, preferably hydrogen, is added as required to the reactors, and preferably
35 350-450 moles of H₂/kmoles of ethylene are added to the reactor producing the LMW fraction and 20-40 moles of

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H₂/kmoles of ethylene are added to the reactor producing the HMW fraction.

As indicated earlier, the catalyst for polymerising the multimodal polyethylene of the invention preferably is a Ziegler-Natta type catalyst. Particularly preferred are catalysts with a high overall activity as well as a good activity balance over a wide range of hydrogen partial pressures. As an example hereof may be mentioned the catalysts disclosed in EP 688794 and in FI 980788.

Such catalysts also have the advantage that the catalyst (procatalyst and cocatalyst) only needs to and, indeed, only should be added in the first polymerisation reactor.

Although the invention has been described above with reference to a specified multimodal polyethylene, it should be understood that this multimodal polyethylene may include various additives such as fillers, etc. as is known and conventional in the art. Further, the pipe made of the specified multimodal polyethylene may be a single-layer pipe or form part of a multilayer pipe including further layers of other pipe materials.

Having thus described the present invention it will now be illustrated by way of non-limiting examples of preferred embodiments in order to further facilitate the understanding of the invention.

25 Example 1

A pipe resin was produced by means of a three-step process in a prepolymerisation loop-reactor followed by first a loop-reactor and then a gas phase-reactor. The split was 2:42:56. No comonomer was used in the two consecutive loop-reactors, while 1-butene was used as comonomer in the HMW-fraction produced in the gas phase-reactor in an amount such that the 1-butene comonomer content of the total resulting polymer was 2.6% by weight. A Ziegler-Natta type catalyst as disclosed in EP 688 794 was used. The M_n of the final polymer was found to be 8500 and the M_w 200000. M_w/M_n thus was 23.5. The density was 941 kg/m³ (ISO 1183 D) and MFR₅ was

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0.85 g/10 min. (ISO 1133, condition T). The processability was measured using a Battenfeldt 1-90-30B extruder, which gave an output of 730 kg/h at a screw speed of 158 rpm. The extruder head temperature was 220°C and the die temperature was 210°C. Under the same conditions a conventional unimodal polyethylene pipe resin (MDPE with a density of 940 kg/m³ and an MFR₅ of 0,85 g/10 min) gave an output of 690 kg/h.

Physical test values were as follows:

10	E-modulus (ISO 527-2/1B)	840 MPa
	Impact strength at 0°C (ISO 179)	16 kJ/m ²
	Pressure test on unnotched	
	32 mm pipe (ISO 1167)	>5000 h at 10.0 MPa/20°C
		>1000 h at 4.6 MPa/80°C
15		>5000 h at 4.0 MPa/80°C
	Pressure test on notched	
	110 mm pipe (ISO 13479)	>5000 h at 4.0 MPa/80°C
	RCP-resistance in the	
	S4-test on 110 mm pipe	T _{crit} = -4°C

20 Exempel 2

A pipe resin was produced using the same reactor configuration as used in example 1. The split was 1:45:54. No comonomer was used in the two consecutive loop reactors, while 1-butene was used in the HMW-fraction produced in the gas phase reactor in an amount such that the 1-butene comonomer content of the total resulting polymer was 1.3% by weight. The same catalyst type was used as in example 1. The M_n of the final polymer was found to be 10500 and the M_w 285000. M_w/M_n thus was 27.

30 The density was 959 kg/m³ and MFR₅ was 0,35 g/10 min.

Physical test values were as follows:

E-modulus (ISO 527-2/1B)	1135 MPa
Impact strength at 0°C (ISO 179)	13.7 kJ/m ²

~~Pressure test on unnotched~~

35	110 mm pipe (ISO 1167)	594 h at 12.4 MPa/20°C
		>10000 h at 5.0 MPa/80°C

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Pressure test on notched
110 mm pipe (ISO 13479)
RCP-resistance in the
S4-test on 110 mm pipe

1500 h at 4.6 MPa/80°C

 $T_{crit} = -7^{\circ}\text{C}$; $P_{crit} > 10$ bar

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CLAIMS

1. A multimodal polyethylene composition for pipes,
5 which multimodal polyethylene has a density of
0.930-0.965 g/cm³ and an MFR₅ of 0.2-1.2 g/10 min,
characterised in that the multimodal poly-
ethylene has an M_n of 8000-15000, an M_w of 180-330 x 10³,
and an M_w/M_n of 20-35, said multimodal polyethylene
10 comprising a low molecular weight (LMW) ethylene homo-
polymer fraction and a high molecular weight (HMW)
ethylene copolymer fraction, said HMW fraction having a
lower molecular weight limit of 3500, and a weight ratio
of the LMW fraction to the HMW fraction of (35-55):(65-
15 45).

2. A multimodal polymer composition as claimed in
claim 1, wherein the multimodal polymer is a bimodal
polyethylene produced by (co)polymerisation in at least
two steps.

20 3. A multimodal polymer composition as claimed in
claim 1, wherein the ethylene copolymer of the HMW
fraction is a copolymer of ethylene and a comonomer
selected from the group consisting of 1-butene,
1-hexene, 4-methyl-1-pentene, and 1-octene.

25 4. A multimodal polymer composition as claimed in
any one of claims 1-3, wherein the amount of comonomer is
0.4-3.5 mol% of the multimodal polymer.

5. A multimodal polymer composition according to any
of claims 1-4, having a weight ratio of the LMW fraction
30 to the HMW fraction of (43-51):(57-49).

6. A multimodal polymer composition as claimed in
any one of claims 1-5, wherein the multimodal polymer has
an MFR₅ of 0.3-1.0 g/10 min.

~~7. A multimodal polymer composition as claimed in~~
35 claim 1, wherein the polymer is obtained by slurry poly-
merisation in a loop reactor of a LMW ethylene homo-

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polymer fraction, followed by gas-phase polymerisation of a HMW ethylene copolymer fraction.

8. A multimodal polymer composition as claimed in claim 7, wherein the slurry polymerisation is preceded by
5 a prepolymerisation step.

9. A multimodal polymer composition as claimed in claim 8, wherein the polymer is obtained by prepolymerisation in a loop reactor, followed by slurry polymerisation in a loop reactor of a LMW ethylene homopolymer
10 fraction, and gas-phase polymerisation of a HMW ethylene copolymer fraction.

10. A multimodal polymer composition as claimed in any one of claims 7-9, wherein polymerisation procatalyst and cocatalyst are added to the first polymerisation
15 reactor only.

11. A multimodal polymer composition as claimed in claim 10, wherein the polymerisation catalyst is a Ziegler-Natta type catalyst.

12. A pipe characterised in that it is a
20 pressure pipe comprising the multimodal polymer composition according to any one of the preceding claims, which pipe withstands a pressure of 8.0 MPa gauge during 50 years at 20°C (MRS8.0).

13. A pipe as claimed in claim 12, wherein the pipe
25 is a pressure pipe withstanding a pressure of 10 MPa gauge during 50 years at 20°C (MRS10.0).

14. A pipe as claimed in claim 12 or 13, wherein the pipe has a rapid crack propagation (RCP) S4-value of -1°C or lower.

30 15. A pipe as claimed in claim 14, wherein the pipe has a rapid crack propagation (RCP) S4-value of -7°C or lower.

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/SE 99/01195

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C08L 23/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C08L, C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5494965 A (ALI HARLIN ET AL), 27 February 1996 (27.02.96), abstract, claims --	1-15
A	WO 9703124 A1 (BOREALIS POLYMERS OY), 30 January 1997 (30.01.97), abstract, claims -- -----	1-11

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

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"O" document referring to an oral disclosure, use, exhibition or other means

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Date of the actual completion of the international search

18 October 1999

Date of mailing of the international search report

20-10-1999

Name and mailing address of the ISA/
Swedish Patent Office
Box 5055, S-102 42 STOCKHOLM
Facsimile No. +46 8 666 02 86

Authorized officer

Hélène Eriksson/EÖ
Telephone No. +46 8 782 25 00

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INTERNATIONAL SEARCH REPORT

Information on patent family members

28/09/99

International application No.

PCT/SE 99/01195

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5494965 A	27/02/96	AT 173484 T CA 2136742 A CN 1106613 A DE 69414667 D,T EP 0642549 A,B ES 2123126 T FI 98819 B,C FI 931343 A NO 944525 A WO 9422948 A	15/12/98 13/10/94 09/08/95 08/04/99 15/03/95 01/01/99 15/05/97 27/09/94 25/11/94 13/10/94
WO 9703124 A1	30/01/97	AU 693784 B AU 6308096 A AU 6374896 A BR 9609604 A BR 9609621 A CA 2225858 A CA 2226549 A CN 1190417 A CN 1195363 A CZ 9800065 A EP 0837905 A,B EP 0837915 A HU 9802544 A JP 10511734 T PL 324435 A PL 325016 A SE 504455 C SE 9502508 A WO 9703139 A	09/07/98 10/02/97 10/02/97 25/05/99 06/04/99 30/01/97 30/01/97 12/08/98 07/10/98 15/04/98 29/04/98 29/04/98 29/03/99 10/11/98 25/05/98 06/07/98 17/02/97 11/01/97 30/01/97

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(51) International Patent Classification ⁶ : C08L 23/04	A1	(11) International Publication Number: WO 00/01765 (43) International Publication Date: 13 January 2000 (13.01.00)
(21) International Application Number: PCT/SE99/01195 (22) International Filing Date: 1 July 1999 (01.07.99) (30) Priority Data: 9802409-4 6 July 1998 (06.07.98) SE (71) Applicant (for all designated States except US): BOREALIS POLYMERS OY [FI/FI]; P.O. Box 330, FIN-06101 Porvoo (FI). (72) Inventors; and (75) Inventors/Applicants (for US only): ASUMALAHTI, Markku [FI/FI]; Louhenkuja 3, FIN-04230 Kerava (FI). ÄÄRILÄÄ, Jari [FI/FI]; Partiomiehentie 1B 31, FIN-06100 Porvoo (FI). PALMROOS, Ari [FI/FI]; Haltijakuja 4F 19, FIN-04230 Kerava (FI). BÄCKMAN, Mats [SE/SE]; Forsstenagatan 4 H, S-416 51 Göteborg (SE). NILSSON, Anette [SE/SE]; Hermans väg 11, S-444 60 Stora Höga (SE). PALMLÖF, Magnus [SE/SE]; Nya Varvet 9, S-426 71 Västra Frölunda (SE). (74) Agent: AWAPATENT AB; P.O. Box 5117, S-200 71 Malmö (SE).		(81) Designated States: AE, AL, AM, AT, AT (Utility model), AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, CZ (Utility model), DE, DE (Utility model), DK, DK (Utility model), EE, EE (Utility model), ES, FI, FI (Utility model), GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (Utility model), SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: POLYMER COMPOSITION FOR PIPES (57) Abstract A multimodal polymer composition for pipes is disclosed. The polymer is a multimodal polyethylene with a density of 0.930–0.965 g/cm ³ , an MFR ₅ of 0.2–1.2 g/10 min, and M _n of 8000–15000, an M _w of 180–330 x 10 ³ , and an M _w /M _n of 20–35, said multimodal polyethylene comprising a low molecular weight (LMW) ethylene homopolymer fraction and a high molecular weight (HMW) ethylene copolymer fraction, said HMW fraction having a lower molecular weight limit of 3500, and a weight ratio of the LMW fraction to the HMW fraction of (35–55) : (65–45).		

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/SE 99/01195

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C08L 23/04

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A	WO 9703124 A1 (BOREALIS POLYMERS OY), 30 January 1997 (30.01.97), abstract, claims -- -----	1-11

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Date of the actual completion of the international search

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Date of mailing of the international search report

20-10-1999

Name and mailing address of the ISA/
Swedish Patent Office
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INTERNATIONAL SEARCH REPORT

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International application No.

PCT/SE 99/01195

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PCT REQUEST

The undersigned requests that the present
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International Application No.

International Filing Date

Name of receiving Office and "PCT International Application"

Applicant's or agent's file reference **2991406**
(if desired)(12 characters maximum)

Box No. I TITLE OF INVENTION
POLYMER COMPOSITION FOR PIPES

Box No. II APPLICANT

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

BOREALIS POLYMERS OY
P O Box 330
FI-06101 PORVOO
Finland

☐ This person is also inventor.

Telephone No.

Facsimile No.

Teleprinter No.

State (that is, country) of nationality: **Finland**

State (that is, country) of residence: **Finland**

This person is applicant for the purposes of: ☐ all designated States ☒ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box

Box No. III FURTHER APPLICANT(S) AND/OR /FURTHER INVENTOR(S)

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

ASUMALAHTI, Markku
Louhenkuja 3
FI-04230 KERAVALA
Finland

This person is:

☐ applicant only
☒ applicant and inventor
☐ inventor only (If this check-box is marked, do not fill in below.)

State (that is, country) of nationality: **Finland**

State (that is, country) of residence: **Finland**

This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☒ the United States of America only ☐ the States indicated in the Supplemental Box

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The person identified below is hereby/has been appointed to act on behalf of the applicant(s) before the competent International Authorities as: ☒ agent ☐ common representative

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AWAPATENT AB
Box 5117
S-200 71 MALMÖ
SWEDEN

Telephone No.

+46 40 98 51 00

Facsimile No.

+46 40 26 05 16

Teleprinter No.

☐ Address for correspondence: Mark this check-box where no agent or common representative is/has been appointed and the space above is used instead to indicate a special address to which correspondence should be sent

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ÄÄRILÄÄ, Jari
Partiomiehentie 1B 31
FI-06100 PORVOO
Finland

This person is:

- ☐ applicant only
☒ applicant and inventor
☐ inventor only (If this check-box is marked, do not fill in below.)

State (that is, country) of nationality: **Finland**

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PALMROOS, Ari
Haltijakuja 4F 19
FI-04230 KERAVA
Finland

This person is:

- ☐ applicant only
☒ applicant and inventor
☐ inventor only (If this check-box is marked, do not fill in below.)

State (that is, country) of nationality: **Finland**

State (that is, country) of residence: **Finland**

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BÄCKMAN, Mats
Forsstenagatan 4 H
S-416 51 GÖTEBORG
Sweden

This person is:

- ☐ applicant only
☒ applicant and inventor
☐ inventor only (If this check-box is marked, do not fill in below.)

State (that is, country) of nationality: **Sweden**

State (that is, country) of residence: **Sweden**

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Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

Nilsson, Anette
Hermans väg 11
S-444 60 STORA HÖGA
Sweden

This person is:

- ☐ applicant only
☒ applicant and inventor
☐ inventor only (If this check-box is marked, do not fill in below.)

State (that is, country) of nationality: **Sweden**

State (that is, country) of residence: **Sweden**

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PALMLÖF, Magnus

Nya Varvet 9

S-426 71 VÄSTRA FRÖLUNDA

Sweden

This person is:

- ☐ applicant only
☒ applicant and inventor
☐ inventor only (If this check-box is marked, do not fill in below.)

State (that is, country) of nationality: Sweden

State (that is, country) of residence: Sweden

This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☒ the United States of America only ☐ the States indicated in the Supplemental Box

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

This person is:

- ☐ applicant only
☐ applicant and inventor
☐ inventor only (If this check-box is marked, do not fill in below.)

State (that is, country) of nationality:

State (that is, country) of residence:

This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box

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Box No. V DESIGNATION OF STATES

The following designations are hereby made under Rule 4.9(a) (mark the applicable check-boxes; at least one must be marked):

Regional Patent

- ☒ **AP** ARIPO Patent: GH Ghana, GM Gambia, KE Kenya, LS Lesotho, MW Malawi, SD Sudan, SZ Swaziland, UG Uganda, ZW Zimbabwe and any other State which is a Contracting State of the Harare Protocol and of the PCT
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- ☒ **EP** European Patent: AT Austria, BE Belgium, CH and LI Switzerland and Liechtenstein, CY Cyprus, DE Germany, DK Denmark, ES Spain, FI Finland, FR France, GB United Kingdom, GR Greece, IE Ireland, IT Italy, LU Luxembourg, MC Monaco, NL Netherlands, PT Portugal, SE Sweden, and any other State which is a Contracting State of the European Patent Convention and of the PCT
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| <input checked="" type="checkbox"/> BA Bosnia and Herzegovina | <input checked="" type="checkbox"/> MG Madagascar |
| <input checked="" type="checkbox"/> BB Barbados | <input checked="" type="checkbox"/> MK The former Yugoslav Republic of Macedonia |
| <input checked="" type="checkbox"/> BG Bulgaria | |
| <input checked="" type="checkbox"/> BR Brazil | <input checked="" type="checkbox"/> MN Mongolia |
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Box No. VI PRIORITY CLAIM				
<input type="checkbox"/> Further priority claims are indicated in the Supplement Box.				
Filing date of earlier application (day/month/year)	Number of earlier application	Where earlier application is:		
		national application: country	regional application:* regional Office	international application: receiving Office
item (1) 6 July 1998 6.7 1998	9802409-4	Sweden		
item (2)				
item (3)				

☒ The receiving Office is requested to prepare and transmit to the International Bureau a certified copy of the earlier application(s) (only if the earlier application was filed with the Office which for the purposes of the present international application is the receiving Office) identified above as item(s): _____

* Where the earlier application is an ARIPO application, it is mandatory to indicate in the Supplemental Box at least one country party to the Paris Convention for the Protection of Industrial Property for which that earlier application was filed (Rule 4.10(b)(ii)). See Supplemental Box.

Box No. VII INTERNATIONAL SEARCHING AUTHORITY

Choice of International Searching Authority (ISA) (if two or more International Authorities are competent to carry out the international search, indicate the Authority chosen; the two-letter code may be used):	Request to use results of earlier search; reference to that search (if an earlier search has been carried out by or requested from the International Searching Authority):		
ISA / SE	Date (day/month/year) 6 July 1998	Number SE 98/00705	Country (or regional Office) Sweden

Box No. VIII CHECK LIST; LANGUAGE OF FILING

This international application contains the following number of sheets: request : 5 description (excluding sequence listing part) : 13 claims : 2 abstract : 1 drawings : sequence listing part of description : Total number of sheets : 21	This international application is accompanied by the item(s) marked below: 1. <input checked="" type="checkbox"/> fee calculation sheet 2. <input type="checkbox"/> separate signed power of attorney 3. <input type="checkbox"/> copy of general power of attorney; reference No., if any: 4. <input type="checkbox"/> statement explaining lack of signature 5. <input type="checkbox"/> priority document(s) identified in Box No. VI as item(s): 6. <input type="checkbox"/> translation of international applications into (language): 7. <input type="checkbox"/> separate indications concerning deposited microorganism or other biological material 8. <input type="checkbox"/> nucleotide and/or amino acid sequence listing in computer readable form 9. <input checked="" type="checkbox"/> other (specify): Copy of Search Report and Official Letter
Figure of the drawings which should accompany the abstract:	Language of filing of the international application: English

Box No. IX SIGNATURE OF APPLICANT OR AGENT

Next to each signature, indicate the name of the person signing and the capacity in which the person signs (if such capacity is not obvious from reading the request).



Erik Wiklund
Authorised Agent

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1. Date of actual receipt of the Purported international application:		
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4. Date of timely receipt of the required Corrections under PCT Article 11(2):		
5. International Searching Authority (if two or more are competent): ISA/	6. <input type="checkbox"/> Transmittal of search copy delayed until search fee is paid.	

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Hakemispäivä: **6.4.98**
Siirretty alkupäivä:
Tullut julkiseksi:

Patentti- ja rekisterihallitus
Arkadiankatu 6 A
00100 HELSINKI

Viitteemme: 46582/BT/TJ

PATENTTIHAKEMUS

Hakija(t)	BOREALIS POLYMERS OY
Kotipaikka	Porvoo maalaiskunta
Osoite	PL 330, 06101 Porvoo

Asiamies:	Berggren Oy Ab, Helsinki
Nimi ja osoite	Jaakonkatu 3 A, 00100 Helsinki

Keksijä(t)	1. LINDROOS, Jarmo
Nimi ja osoite	Kissansalmentie 16 a, 06750 Tolkkinen
	2. JOHANSSON, Solveig
	Haglingevägen 1, S-44447 Stenungsund, Ruotsi
	3. WALDVOGEL, Päivi
	Päiväläispolku 12 c, 06450 Porvoo

Keksinnön nimitys	Olefiinipolymeroinnin katalysaattorikomponentti, sen valmistus ja käyttö - Katalysatorkomponent för polymerisation av olefiner, dess framställning och användning
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Etuoikeus	
Maa, numero ja päivä	Vastaavaa hakemusta ei ole aikaisemmin jätetty muissa maissa.

Pyydämme, että hakemus käsitellään englanninkielisten asiakirjojen perusteella PA 3§:n 2 momentin mukaisesti.

Helsingissä, 6.4.1998

Valtakirjalla
BERGGREN OY AB

Liitteet:

Hakemuskirjan jäljennös	
Selitys englanniksi	3 kpl:na
Vaatimukset englanniksi	3 "
Tiivistelmä englanniksi	3 "
Siirtokirja	jät.myöh.
Valtakirja	jät.myöh.

Maksut:

Perusmaksu 1200 mk
Lisämaksu jokaisesta 10 ylittävästä patenttivaatimuksesta 3960 mk (11-43)
Viitejulkaisumaksu 160 mk

Olefin polymerization catalyst component, its preparation and use

The invention relates to a process for the preparation of a high activity catalyst component for the production of olefin polymers. The invention also relates to a
5 procatalyst prepared by said process and the use of such a procatalyst in the polymerization of olefins.

Olefinic unsaturated monomers such as ethylene can often be polymerized in the presence of a catalyst composition, which has essentially two components: a compound of a transition metal belonging to one of groups 4 to 6 of the Periodic
10 Table of Elements (Hubbard, IUPAC 1990) which is often called a procatalyst, and a compound of a metal belonging to any of groups 1 to 3 of said Table which is often called a cocatalyst. This kind of Ziegler-Natta catalyst composition has been further developed by depositing the procatalyst on a more or less inert and particulate support and by adding to the catalyst composition in the stages of its
15 preparation several additives, among others electron donating compounds. These compounds have improved the polymerization activity of the catalyst, the operating life and other properties of the catalyst composition and first of all properties of the polymers which are obtained by means of the catalyst composition.

When ethylene polymers are produced, the polymer molecules formed are not
20 similar by molecular weight, but a mixture having a narrow or broad molecular weight distribution and an average molecular weight is developed. Different average molecular weights can be defined for the polymer mixtures to describe the most common molecular weight by giving the top value of the distribution, and also several indices has been developed to describe the breadth of the distribution. For
25 controlling the molecular weight a so called chain transfer agent can be added to the polymerization reaction mixture. In order to obtain polymer products having different molecular weights, different amounts of the chain transfer agent for controlling the molecular weight must be fed into the polymerization reaction mixture. The most usual and preferable chain transfer agent is hydrogen, because
30 when using it no foreign atoms or atom groups are left in the growing molecule, which would cause inconveniencies for the polymerization process or disadvantageous properties of the polymer produced.

How well the molecular weight of the produced polymer varies as function of the hydrogen amount, i.e. how much the so called hydrogen sensibility changes, greatly

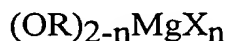
depends on the catalyst composition. Generally the problem is, that in polyethylene production the polymerization activity of a certain catalyst composition in the production of a polymer having high molecular weight is higher, usually many times, even ten times higher, than in the production of a polymer having low molecular weight.

This absence of catalyst activity balance is a common drawback for all prior art catalysts today. The imbalance shows up when, using prior art catalysts, a drastic drop in the productivity of the catalysts occurs when going from polymerization conditions giving high molecular weight polymers (low melt flow rate) to polymerization conditions giving low molecular weight polymers (high melt flow rate). Even if this kind of a commercial catalyst can have a quite good productivity at a polymer melt flow rate (MFR, defined according to standard ISO 1133) of 1, there is often only 10% left of the productivity when producing a MFR of 500. Thus it is desirable to provide a catalyst system having a high activity which is independent from the molar mass of the polymer under formation.

EP-A-32307 discloses a procatalyst that has been prepared by treating an inorganic support like silica with a chlorination agent like ethyl aluminium dichloride which support is contacted with a magnesium alkyl compound like butylethyl magnesium, and with titanium tetrachloride (see claim 1, example 1, table 1).

EP-A-688 794 discloses a process for the production of a high activity procatalyst, wherein an inorganic support is reacted with an alkyl metal chloride, the first reaction product is reacted with a compound containing hydrocarbonyl and hydrocarbonyl oxide linked to magnesium, and the obtained second reaction product is contacted with a titanium chloride compound. The obtained procatalyst has good activity both at high and low MFR polymerization conditions, but it has the drawback of giving an inhomogeneous ethylene polymer product. The results are gels and white dots are the polymer material. These inhomogeneities have detrimental effect on the mechanical properties of polyethylene film.

The drawbacks encountered by EP-A-688 794 have now been eliminated by a modified process, characterized by the steps of reacting a support comprising a magnesium halide compound having the formula (1):



(1)

wherein each same or different R is a C₁-C₂₀ alkyl or a C₇-C₂₆ aralkyl, each same or different X is a halogen, and n is an integer 1 or 2,

an alkyl metal halide compound having the formula (2):



wherein Me is B or Al, each same or different R^1 is a C_1 - C_{10} alkyl, each same or different X^1 is a halogen, n^1 is an integer 1 or 2, and m^1 is an integer 1 or 2,

- 5 a magnesium composition containing magnesium bonded to a hydrocarbyl and magnesium bonded to a hydrocarbyl oxide, said magnesium composition having the empirical formula (3):



- 10 wherein each same or different R^2 is a C_1 - C_{20} alkyl, each same or different R^3 is a C_1 - C_{20} alkyl or a C_1 - C_{20} alkyl having a hetero element, and n^2 is between 0.01 and 1.99, and

a titanium halide compound having the formula (4):



- 15 wherein each same or different R^4 is a C_1 - C_{20} alkyl, each same or different X^2 is a halogen, n^3 is 0 or an integer 1-3, and Ti is quadrivalent titanium.

- By "magnesium composition" above is meant a mixture or a compound. Note that formula (3) is an empirical formula and expresses the molar amounts of alkyl R^2 and alkoxy OR^3 relative to the amount of magnesium Mg, which has been defined as 1, and differs from formulas (1), (2) and (4), which are essentially structural formulas and express the molecular structure of reagents (1), (2) and (4).

- 20 A procatalyst has now been discovered by which ethylene homopolymers or copolymers having low or high molecular weight can be produced with an even and high activity as well as a homogenous consistence. Independently of the amount of hydrogen introduced into the polymerization reactor, a balance of the activities and a homogenous ethylene polymer product are achieved.

- 30 The unique feature of the catalyst according to the invention now lies in its good balance in activity and a homogenous product in a very wide range of molar mass regulating hydrogen partial pressures used in the polymerization. It is thus possible to carry out an ethylene polymerization by the use of this catalyst at high and low melt flow and still have very similar high productivity as well as a homogenous, gel

free product. This MFR/activity balance renders the catalyst universally applicable for most types of PE resins in all polymerization processes using heterogeneous catalyst systems.

Preferably, the claimed process comprises the subsequent steps of:

- 5 a) providing said support comprising a magnesium halide compound having the formula (1),
- b) contacting said support comprising a magnesium halide compound having the formula (1) with said alkyl metal halide compound having the formula (2), to give a first product,
- 10 c) contacting said first product with said magnesium composition containing magnesium bonded to a hydrocarbyl and magnesium bonded to a hydrocarbyl oxide and having the empirical formula (3), to give a second product, and
- d) contacting said second product with said titanium halide compound having the formula (4).
- 15 The support used in the process is preferably in the form of particles, the size of which is from about 1 μm to about 1000 μm , preferably about 10 μm to about 100 μm . The support material must have a suitable particle size distribution, a high porosity and a large specific surface area. A good result is achieved if the support material has a specific surface area between 100 and 500 m^2/g support and a pore
- 20 volume of 1-3 ml/g support.

The above catalyst components (2) to (4) are reacted with a suitable catalyst support. If the catalyst components (2) to (4) are in the form of a solution of low viscosity, good catalyst morphology and therewith good polymer morphology can be achieved.

-
- 25 ~~It is advantageous if in the magnesium halide compound having the formula (1), R is a $\text{C}_1\text{-C}_{20}$ alkoxy or a $\text{C}_7\text{-C}_{26}$ aralkoxy. However, it is preferable, if said compound (1) is a magnesium dihalide, most preferably MgCl_2 . for example, the support may comprise solid MgCl_2 , either alone as a powder, or as a powder mixture with other inorganic powders.~~
-

- 30 According to another embodiment of the invention, the support comprising a magnesium halide compound having the formula (1) comprises an inorganic oxide. Several oxides are suitable, but silicon, aluminium, titanium, chromium and

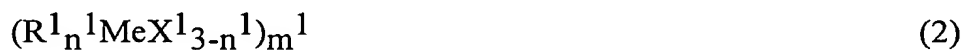
zirconium oxide or mixtures thereof are preferred. The most preferred inorganic oxide is silica, alumina, silica-alumina, magnesia and mixtures thereof, uttermost preferably silica. The inorganic oxide can also be chemically pretreated, e.g. by silylation or by treatment with aluminium alkyls.

- 5 It is good to dry the inorganic oxide before impregnating it by other catalyst components. A good result is achieved if the oxide is heat-treated at 100 °C to 900 °C for a sufficient time, and thereby the surface hydroxyl groups, in the case of silica, are reduced to below 2 mmol/g SiO₂.

As was said above, the support may be a mixture of said magnesium halide
10 compound (1) and another solid powder, which preferably is an inorganic oxide. According to another aspect of the invention, the support comprises particles having a core comprising said inorganic oxide and a shell comprising said magnesium halide compound having the formula (1). Then, the support comprising a magnesium halide compound having the formula (1) and an inorganic oxide can
15 conveniently be prepared by treating particles of the inorganic oxide with a solution of the magnesium halide and removing the solvent by evaporation.

When using a support containing both said magnesium halide compound (1) and another component, the amount of magnesium halide compound (1) is such that the support contains from 1 to 20 % by weight, preferably from 2 to 6 % by weight,
20 of magnesium Mg.

The invention further comprises a step of reacting an alkyl metal halide compound of the formula (2):



wherein Me is B or Al, each same or different R¹ is a C₁-C₁₀ alkyl, each same or
25 different X¹ is a halogen, n¹ is an integer 1 or 2, and m¹ is an integer 1 or 2. In formula (2), Me is preferably Al. Each same or different R¹ is preferably a C₁-C₆ alkyl, and, independently, the preferred same or different halogen X¹ is chlorine. n¹ is preferably 1 and m¹ is preferably the integer 1 or 2. Most preferably, the alkyl metal halide compound having the formula (2) is an alkyl aluminium dichloride,
30 e.g. ethylaluminium dichloride (EADC).

The alkyl metal halide compound is preferably deposited on the support material. An even deposition is achieved if the viscosity of the agent or its solution is below 10 mPa*s at the temperature applied. To achieve this low viscosity the alkyl metal

halide agent can be diluted by a non-polar hydrocarbon. The best deposition is however achieved if the total volume of the deposited alkyl metal halide solution is not exceeding the pore volume of the support, or if the excess of diluting hydrocarbon is evaporated away after the deposition of the alkyl metal halide. A
 5 good choice is to use a 5-25% hydrocarbon solution of ethyl aluminium dichloride. The chemical addition times and the addition techniques are preferably adjusted to give an even distribution of the chemical in the support material.

In the above mentioned preferred order of reaction steps a) to d), step b) can advantageously be performed so that undiluted alkyl metal halide (2) is used to treat
 10 the support comprising a magnesium halide compound having the formula (1). Alternatively, the support is contacted with a solution of the alkyl metal halide compound having the formula (2) in an essentially non-polar solvent, preferably a non-polar hydrocarbon solvent, most preferably a C₄-C₁₀ hydrocarbon. The concentration of the alkyl metal halide compound having the formula (2) in said
 15 non-polar solvent is usually 1-80% by weight, preferably 5-40% by weight, most preferably 10-30% by weight. Advantageously, the support is contacted with a solution of said alkyl metal halide compound (2) in a ratio mol of the alkyl metal halide compound (2) to grams of the support of between about 0.01 mmol/g and about 100 mmol/g, preferably about 0.5 mmol/g and about 2.0 mmol/g. The amount
 20 of reactants can also be expressed as molar ratio, whereby it is advantageous, if the molar ratio of said alkyl metal halide compound (2) to said magnesium halide compound (1) of the support is between about 0.01 mol/mol to about 100, preferably about 0.1 mol/mol to about 10, most preferably from about 0.2 to about 3.0.

25 In step b), the temperature of said contacting is e.g. 5-80 °C, preferably 10-50 °C, most preferably 20-40°C. The duration of said contacting is 0.1-3 h, preferably 0.5-1.5 h.

30 In the claimed process, the ~~magnesium composition containing magnesium bonded~~ to a hydrocarbyl and magnesium bonded to a hydrocarbyl oxide having the empirical formula (3), each same or different R² is preferably a C₂-C₁₀ alkyl, most preferably a C₂-C₈ alkyl. Each same or different R³ is preferably a C₃-C₂₀ alkyl, more preferably a branched C₄-C₁₀ alkyl, most preferably a 2-ethyl-1-hexyl or a 2-propyl-1-pentyl.

35 The magnesium composition containing magnesium bonded to a hydrocarbyl and magnesium bonded to a hydrocarbyl oxide having the empirical formula (3) can

also be expressed by its preparation. According to one embodiment of the invention, it is a contact product of a dialkyl magnesium having the formula (5):



wherein each same or different R^2 is defined as above, and an alcohol. Preferably, the dialkyl magnesium having the formula (5) is dibutyl magnesium, butyl ethyl magnesium or butyl octyl magnesium.

The magnesium composition can also be defined that the magnesium composition containing magnesium bonded to a hydrocarbyl and magnesium bonded to a hydrocarbyl oxide having the empirical formula (3) is a contact product of a dialkyl magnesium and an alcohol having the formula (6):



wherein each same or different R^3 is the same as above. Preferably, the alcohol having the formula (6) is a 2-alkyl alkanol, preferably 2-ethyl hexanol or 2-propyl pentanol. It was found, that such branched alcohols gave better results than linear alcohols.

Preferably, the magnesium composition containing magnesium bonded to a hydrocarbyl and magnesium bonded to a hydrocarbyl oxide having the empirical formula (3) is a contact product of a dialkyl magnesium and an alcohol in a molar ratio alcohol to dialkyl magnesium of 0.01-100 mol/mol, preferably 1.0-5.0 mol/mol, more preferably 1.7-2.0 mol/mol, most preferably 1.8-1.98 mol/mol. The dialkyl magnesium and the alcohol are conveniently contacted by adding the alcohol to a solution of said dialkyl magnesium in an organic solvent, e.g. a $\text{C}_4\text{-C}_{10}$ hydrocarbon. Then, the concentration of the solution is preferably between 1 and 50% by weight, most preferably between 10 and 30% by weight. The contacting temperature between the dialkyl magnesium and the alcohol is preferably 10-50 °C, preferably from about 20 °C to about 35 °C.

In step c) of the above mentioned preferred order a) \mapsto d) of the claimed process, the contacting product of the support with the alkyl metal halide compound (2) (= said first product) is contacted with said magnesium composition containing magnesium bonded to a hydrocarbyl and magnesium bonded to a hydrocarbyl oxide and having the empirical formula (3).

Preferably, said first product is contacted with said magnesium composition (3) in a ratio moles of magnesium/g of the support of between 0.001-1000 mmol/g, preferably 0.01-100 mmol/g, most preferably 0.1-10 mmol/g (g of the support means, in the case of said first reaction product, the support which was used as starting material for the first reaction product).

A good deposition of said magnesium composition as a solution is achieved if the volume of the magnesium composition (3) solution is about two times the pore volume of the support material. This is achieved if the concentration of the composition in a hydrocarbon solvent is between 5-60% in respect of the hydrocarbon used. When depositing the magnesium composition on the support material its hydrocarbon solution should have a viscosity that is lower than 10 mPa*s at the temperature applied. The viscosity of the magnesium complex solution can be adjusted for example by the choice of the group R^4 in the formula (3), by the choice of the concentration of the hydrocarbon solution, by the choice of the ratio between the magnesium alkyl and the alcohol or by using some viscosity lowering agent. The titanium compound can be added to the support material with or without a previous drying of the catalyst to remove the volatile hydrocarbons. Remaining hydrocarbons can if desired be removed by using slight underpressure, elevated temperature or nitrogen flash.

In the claimed process, the transition metal compound is a titanium halide compound having the formula (4). R^4 is preferably a C_2 - C_8 alkyl, most preferably a C_2 - C_6 alkyl. X^2 is preferably chlorine and, independently, n^3 is preferably 0. Said titanium halide compound having the formula (4) is advantageously titanium tetrachloride.

According to one embodiment of the invention, in addition to said titanium compound having the formula (4), a titanium compound having the formula (7):



wherein each same or different R^5 is a C_1 - C_{20} alkyl, preferably a C_2 - C_8 alkyl, most preferably a C_2 - C_6 alkyl, each same or different X^3 is a halogen, preferably chlorine, n^4 is an integer 1-4, and Ti is quadrivalent titanium, is reacted. The titanium compound (7) always has at least one alkoxy group, which helps dissolving the titanium compound (4) which does not necessary have alkoxide, into an organic solvent before the contacting. Naturally, the more alkoxide groups compound (4)

has, the less is the need for compound (7). If compound (7) is used, the preferable combination is that of titanium tetrachloride and a titanium tetra C₁-C₆-alkoxide.

In step d) of the preferred step sequence a) \mapsto d), said second product is advantageously contacted with the titanium compound having the formula (4) in a ratio moles of said titanium compound/g of the support of 0.01-10 mmol/g, preferably 0.1-2 mmol/g. Preferably, said second reaction product is contacted with said titanium compound (4) in a ratio moles of said titanium compound (4)/total moles of the magnesium of 0.05-2 mol/mol, preferably 0.1-1.2 mol/mol, most preferably 0.2-0.7 mol/mol. The temperature is usually 10-80 °C, preferably 30-60 °C, most preferably from about 40 °C to about 50 °C, and the contacting time is usually 0.5-10 h, preferably 2-8 h, most preferably from about 3.5 h to about 6.5 h.

Above, the process for the preparation of a high activity catalyst component for the production of olefin polymers of different molecular weight and homogenous consistence, have been described in detail. The invention also relates to such a high activity catalyst component. The suitability for both low and high molecular weight polymerization means, that the claimed catalyst component has high activity both when producing low melt flow rate ethylene polymer and high melt flow rate polymer. High molecular weight polymer has high melt viscosity, i.e. low melt flow rate, and low molecular weight polymer has low melt viscosity, i.e. high melt flow rate.

Simultaneously or separately, it preferably produces ethylene homopolymer and copolymer with low gel content. Most preferably it produces ethylene homopolymer having a Gel number, measured at specified test conditions, of approximately 0/0 1/m². This means, that by the standards used, the claimed catalyst components can be used to produce totally homogenous (gelless) low and high molecular weight ethylene polymer.

The invention also relates to the use of a catalyst component according to the invention in the polymerization of olefins, preferably in the polymerization of ethylene homopolymers and copolymers. The advantage of the use is based on the fact that the claimed catalyst is suitable for both low molecular weight and high molecular weight ethylene polymerization and that the ethylene polymer produced is of high quality.

In the polymerization, said alkyl metal halide compound of the formula (2) can, if used, act completely or partially as a cocatalyst. However, it is preferable to add a cocatalyst having the formula (9):



- 5 wherein R^6 is a C_1 - C_{20} alkyl, preferably a C_1 - C_{10} alkyl, most preferably a C_2 - C_6 alkyl such as ethyl, X is a halogen, preferably chlorine, n is 1 to 3, more preferably 2 or 3, most preferably 3, to the polymerization mixture. The cocatalyst having the formula (9) can be used irrespectively of whether said alkyl metal halide compound (2) is used or not.

10 Experimental Part

Some Factors Influencing the Gel Level

- Those familiar with the art know that the gel level is influenced by two properties of the polymer the average molecular weight (for which the melt flow rate, or MFR, is an often used measure) and the broadness of the molecular weight distribution (for
15 which the shear thinning index, or SHI, and the flow rate ratio, or FRR, are often used measures). A high molecular weight (or, a low MFR) usually results a higher gel level than a low molecular weight (or, a high MFR). Also, a broad molecular weight distribution (or, a high SHI or FRR) usually results a higher gel level than a narrow molecular weight distribution (or, a low SHI).

20 Film Blowing

Pelletized material samples were blown to a film on a Collin film line. The film blowing conditions were:

Die diameter 30 mm

Die gap 0.75 mm

- 25 Blow-up ratio 3.0
-

Determination of the Gel Level

- A sample of the size 210 mm x 297 mm was cut from a film blown on the Collin line. The film sample was put into a gel scanner, which classifies the gels according
30 to their size. The scanner gives the number of gels in three size classes, < 0.3 mm, 0.3...0.7 mm and > 0.7 mm. Generally the number of gels in the smallest class can

be affected by different random factors, so often only the numbers of the intermediate (0.3...0.7 mm) and large (> 0.7 mm) gels are given.

Determination of the Dispersion of the Black Pellets

5 The dispersion indicates the homogeneity of the black samples in a similar fashion as the gel level indicates the homogeneity of the film samples. It is measured from the black pellets according to the ISO/DIS 11420 method as follows:

10 Six pellets are cut using a microtome to 20 μm cuts. Using an optical microscope, the white spots seen in the sample are then measured and classified according to their size. The average number of white spots in each size class is calculated. An ISO value indicating the dispersion is attributed to the material. A high ISO rating denotes a poor homogeneity (large inhomogeneities).

Examples

Preparation of Complex 1

15 7.9 g (60.8 mmol) of 2-ethyl-1-hexanol was added slowly to 27.8 (33.2 mmol) of 19.9% butyl-octyl-magnesium. The reaction temperature was kept under 35 °C. This complex was used in the following catalyst preparations. 2-ethyl-1-hexanol/butyl-octyl-magnesium ratio is 1.83:2.

Preparation of Complex 2

20 8.6 g (66.4 mmol) of 2-ethyl-1-hexanol was added slowly to 27.8 (33.2 mmol) of 19.9% butyl-octyl-magnesium. The reaction temperature was kept under 35 °C. This complex was used in the following catalyst preparations. 2-ethyl-1-hexanol/butyl-octyl-magnesium ratio is 2:1.

Comparative Example 1:

Production of the Film Material

25 The polymer samples were produced in a continuously operating pilot plant as follows:

The catalyst used in this example was one known in the art, prepared according to patent application EP-A-688794 on a 40 μm silica carrier.

The catalyst was fed into a 50 dm³ loop prepolymerization reactor, where a small amount of polymer was formed on the catalyst particles. The slurry containing the prepolymer was taken out of the reactor and passed into a 500 dm³ loop reactor. There the reactor conditions were set so that ethylene homopolymer with MFR₂ = 500 was formed at a rate of about 25 kg/h. The polymer slurry was taken out of the loop reactor into a flash unit, where the hydrocarbons were separated from the polymer.

The polymer was then passed into a gas phase reactor where the polymerization was continued at a rate of about 35 kg/h. The reactor conditions were set so that MFR₂₁ of the polymer collected from the reactor was about 9 and the density about 946 kg/m³.

The powder was then collected and blended with additives after which it was pelletized. A film was then blown from a pellet sample and the gel level was determined as described above. Table 1 shows some data of the material.

15 Comparative Example 2 (Catalyst APS 12 µm)

6.0 g (1.6 mmol/g carrier) of 20% EADC was added to 5.9 g of Sylopol 2212 silica carrier. The mixture was stirred for one hour at 30 °C. 8.9 g (1.4 mmol/g carrier) of complex prepared according to complex preparation was added after which the mixture was stirred for 4 hours at 35-45 °C. 0.76 g (0.7 mmol/g carrier) of TiCl₄ was added and the mixture was stirred for 5 hours at 45 °C. The catalyst was dried at 45-80 °C for 3 hours.

Composition of the catalyst was: Al 2.4%, Mg 2.0%, Ti 2.0%, Cl 12.5%.

The polymer was prepared as in Comparative example 1.

Comparative Example 3

25 Production of the Pipe Material (POKO lot 1976):

The material was produced according to Comparative Example 1, except that a catalyst was prepared on a 20 µm silica carrier. Also, the material targets were changed to some extent. In the first stage, material having MFR₂ = 300 was produced at a rate of 32 kg/h. The gas phase reactor was operated so that the production was 39 kg/h, MFR₂₁ of the final material was 9 and density was 948. The polymer was then blended with additives including an additive containing carbon black to give the material a black colour. The material was then pelletized.

The dispersion was then determined from the black pellets according to the procedure described earlier. Table 1 shows some data of the material.

Example 1 (Catalyst APS 11 μm)

3.7 g (1.0 mmol/g carrier) of 20% EADC was added to 5.9 g of Sylopol 5510 silica/MgCl₂ carrier and the mixture was stirred for one hour at 30 °C. 5.7 g (0.9 mmol/g carrier) of complex prepared according to complex preparation was added and the mixture was stirred for 4 hours at 35-45 °C. 0.6 g (0.55 mmol/g carrier) of TiCl₄ was added and the mixture was stirred for 5 hours at 45 °C. The catalyst was dried at 45-80 °C for 3 hours.

10 Composition of the catalyst was: Al 1.8%, Mg 3.9%, Ti 2.1%, Cl 18.5%.

The polymerization was performed as in Comparative example 1.

Example 2

Production of the Film Material

15 The material was produced according to Comparative Example 1, except that an inventive catalyst prepared on a 29 μm carrier was used. Table 1 shows some data of the material.

Example 3

Production of the Pipe Material

20 The material was produced according to Comparative Example 3, except that an inventive catalyst prepared on a 20 μm carrier was used. Table 1 shows some data of the material.

Polymerization Results

The catalysts have been tested in Borstar bimodal Loop-Gas-phase process under fixed split and loop melt index.

Table 1. Polymerization and Analysis Results Obtained with Different Catalysts

	CE1	CE2	CE3	Ex 1	Ex 2	Ex 3
Productivity in loop	1.8	5.0		5.0	3.8	
Loop MFR ₂	520	514	300	650	430	323
Final MFR ₂₁	9.7	6.6	9.5	6.3	6.1	9.2
Final density	945.5	946.5	949 ¹	945.5	946.2	949 ¹
SHI _{5/300}	87.5	61.0	40.4 ²	90.2	111	56.6 ²
Gels (0.3...0.7/>0.7)	50/0	300/0		0/0	0/0	
Dispersion <30/30...60/60... 80/>80 μ m			14/2/0.3/0.8			17/2/0/0.2
ISO rating			5.5			3.0

¹ Base resin density, not including carbon black

5 ² SHI_{2.7/210}

Flow rate ratio (FRR) has been calculated as a ratio of two MFR values measured using different loads, $FRR_{21/5} = MFR_{21}/MFR_5$.

10 The number of gels were calculated from film blown to film with Collin line. Comparative results to Collin film line were also obtained from the film analysis with Alpine and Reifenhauser film lines.

The representative polymer lots were characterized by rheology, where SHI_{5/300} comparison is done to polymer with same molecular weight.

15 Measurements were made on Rheometrics RDA II at 190 °C. Complex viscosity (η^*) together with storage modulus (G') and loss modulus (G'') as a function of frequency (ω) or complex modulus (G^*) were obtained.

Complex viscosity (η^*) as a function of complex modulus (G^*) corresponds viscosity as a function of shear stress and its shape is independent of MW. SHI calculated from this function can be used as a measure of MWD.

$$SHI_{5/300} = \eta_{5kPa} / \eta_{300kPa},$$

20 where η_{5kPa} and η_{300kPa} are η^* at a constant G^* of 5 kPa and 300 kPa, respectively.

Claims

1. A process for the preparation of a high activity catalyst component for the production of olefin polymers, **characterized** in that it comprises the steps of reacting:

- 5 a support comprising a magnesium halide compound having the formula (1):



wherein each same or different R is a C₁-C₂₀ alkyl, a C₇-C₂₆ aralkyl, a C₁-C₂₀ alkoxy or a C₇-C₂₆ aralkoxy, each same or different X is a halogen, and n is an integer 1 or 2,

- 10 an alkyl metal halide compound having the formula (2):



wherein Me is B or Al, each same or different R¹ is a C₁-C₁₀ alkyl, each same or different X¹ is a halogen, n¹ is an integer 1 or 2, and m¹ is an integer 1 or 2,

- 15 a magnesium composition containing magnesium bonded to a hydrocarbyl and magnesium bonded to a hydrocarbyl oxide, said magnesium composition having the empirical formula (3):



wherein each same or different R² is a C₁-C₂₀ alkyl, each same or different R³ is a C₁-C₂₀ alkyl, n² is between 0.01 and 1.99, and

- 20 a titanium halide compound having the formula (4):



wherein each same or different R⁴ is a C₁-C₂₀ alkyl, each same or different X² is a halogen, n³ is 0 or an integer 1-3, and Ti is quadrivalent titanium.

- 25 2. A process according to claim 1, **characterized** in that it comprises the subsequent steps of:

a) providing said support comprising a magnesium halide compound having the formula (1),

b) contacting said support comprising a magnesium halide compound having the formula (1) with said alkyl metal halide compound having the formula (2), to give a first product,

5 c) contacting said first product with said magnesium composition containing magnesium bonded to a hydrocarbyl and magnesium bonded to a hydrocarbyl oxide and having the empirical formula (3), to give a second product, and

d) contacting said second product with said titanium halide compound having the formula (4).

10 3. A process according to claim 1 or 2, **characterized** in that said support is in the form of particles, the sized of which is from about 1 μm to about 1000 μm , preferably from about 10 μm to about 100 μm .

4. A process according to claim 1, 2 or 3, **characterized** in that said magnesium halide compound having the formula (1) is a magnesium dihalide, preferably MgCl_2 .

15 5. A process according to any of claim 1-4, **characterized** in that said support comprising a magnesium halide compound having the formula (1) comprises an inorganic oxide.

20 6. A process according to any of claims 1-5, **characterized** in that said inorganic oxide is an inorganic oxide having surface hydroxyls, such as silica, alumina, silica-alumina, magnesia and mixtures thereof, preferably silica.

7. A process according to any preceding claim, **characterized** in that said support comprises particles having a core comprising said inorganic oxide and a shell comprising said magnesium halide compound.

25 8. A process according to claim 5, 6 or 7, **characterized** in that in said support, the amount of said magnesium halide compound having the formula (1), expressed as per cent magnesium Mg calculated on the weight of the support, is 1-20%, preferably 2-6%.

30 9. A process according to any preceding claim, **characterized** in that in said alkyl metal halide having the formula (2), independently, Me is Al, each same or different R^1 is a C_1 - C_6 alkyl, each same or different X^1 is a chlorine, n^1 is 1, and m^1 is an integer 1 or 2.

10. A process according to claim 9, **characterized** in that said alkyl metal halide compound having the formula (2) is an alkyl aluminium dichloride, e.g. ethyl-aluminium dichloride.
- 5 11. A process according to any of claims 2 to 10, **characterized** in that in step b), said support comprising a magnesium halide compound having the formula (1) is contacted with a solution of said alkyl metal halide compound having the formula (2) in an essentially non-polar solvent, preferably a non-polar hydrocarbon solvent, most preferably a C₄-C₁₀ hydrocarbon.
- 10 12. A process according to claim 11, **characterized** in that the concentration of said alkyl metal halide compound having the formula (2) in said non-polar solvent is 1-80% by weight, preferably 5-40% by weight, most preferably 10-30% by weight.
- 15 13. A process according to claim 11 or 12, **characterized** in that the total volume of the alkyl metal halide compound (2) solution is not exceeding the pore volume of the support.
- 20 14. A process according to any of claims 2 to 12, **characterized** in that in step b), said support comprising a magnesium halide compound having the formula (1) is contacted with a solution of said alkyl metal halide compound having the formula (2) in a ratio moles of said alkyl metal halide to grams of said support of between about 0.01 mmol/g and about 100 mmol/g, preferably about 0.5 mmol/g and about 2.0 mmol/g.
- 25 15. A process according to any of claims 2 to 14, **characterized** in that in step b), said support comprising a magnesium halide compound having the formula (1) is contacted with a solution of said alkyl metal halide compound having the formula (2) in a molar ratio of said alkyl metal halide compound (2) to said magnesium halide compound (1) of between about 0.01 and about 100 mol/mol, preferably about 0.1 mol/mol and about 10 mol/mol, most preferably about 0.2 and about 3.0 mol/mol.
- 30 16. A process according to any preceding claim, **characterized** in that in said magnesium composition containing magnesium bonded to a hydrocarbyl and magnesium bonded to a hydrocarbyl oxide having the empirical formula (3), each same or different R² is a C₂-C₁₀ alkyl.

17. A process according to any preceding claim, **characterized** in that in said magnesium composition containing magnesium bonded to a hydrocarbyl and magnesium bonded to a hydrocarbyl oxide having the empirical formula (3), each same or different R^3 is a C_3 - C_{20} alkyl, preferably a branched C_4 - C_{10} alkyl, most preferably a 2-ethyl-1-hexyl or a 2-propyl-1-pentyl.

18. A process according to any preceding claim, **characterized** in that said magnesium composition containing magnesium bonded to a hydrocarbyl and magnesium bonded to a hydrocarbyl oxide having the empirical formula (3) is a contact product of a dialkyl magnesium having the formula (5):



wherein each same or different R^2 is defined as above, and an alcohol.

19. A process according to claim 18, **characterized** in that said dialkyl magnesium having the formula (5) is dibutyl magnesium, butyl ethyl magnesium or butyl octyl magnesium.

20. A process according to any preceding claim, **characterized** in that said magnesium composition containing magnesium bonded to a hydrocarbyl and magnesium bonded to a hydrocarbyl oxide having the empirical formula (3) is a contact product of a dialkyl magnesium and an alcohol having the formula (6):



wherein each same or different R^3 is the same as above.

21. A process according to claim 20, **characterized** in that said alcohol having the formula (6) is a 2-alkyl alkanol, preferably 2-ethyl hexanol or 2-propyl pentanol.

22. A process according to any of claims 18-21, **characterized** in that said ~~magnesium composition containing magnesium bonded to a hydrocarbyl and~~ magnesium bonded to a hydrocarbyl oxide having the empirical formula (3) is a contact product of a dialkyl magnesium and an alcohol in a molar ratio alcohol to dialkyl magnesium of 0.01-100 mol/mol, preferably 1.0-5.0 mol/mol, more preferably 1.7-2.0 mol/mol, most preferably 1.8-1.98 mol/mol.

23. A process according to any of claims 2-22, **characterized** in that in step c), said first product is contacted with said magnesium composition containing

magnesium bonded to a hydrocarbyl and magnesium bonded to a hydrocarbyl oxide and having the empirical formula (3).

24. A process according to any of claims 2-23, **characterized** in that in step c), said support or, optionally, said first reaction product, is contacted with said
5 magnesium composition containing magnesium bonded to a hydrocarbyl and magnesium bonded to a hydrocarbyl oxide and having the empirical formula (3) in a ratio moles of magnesium/g of the support of between 0.001-1000 mmol/g of the support, preferably 0.01-100 mmol/g of the support, most preferably 0.1-10 mmol/g of the support. (g of the support means, in the case of said first reaction product, the
10 support which was used as starting material for the first reaction product.)
25. A process according to any of claims 2-24, **characterized** in that in step c), said support or said first product is contacted with a solution of said magnesium composition (3) in a hydrocarbon.
26. A process according to claim 25, **characterized** in that the concentration of
15 said solution is 5-60% by weight.
27. A process according to claims 25 or 26, **characterized** in that the volume of said solution is about two times the pore volume of the support or said first product.
28. A process according to any preceding claim, **characterized** in that in said titanium halide compound having the formula (4), R^4 is a C_2 - C_8 alkyl, preferably a
20 C_2 - C_6 alkyl.
29. A process according to any preceding claim, **characterized** in that in said titanium halide compound having the formula (4), X^2 is chlorine.
30. A process according to any preceding claim, **characterized** in that in said titanium halide compound having the formula (4), n^3 is 0.
31. A process according to any preceding claim, **characterized** in that said
25 titanium halide compound having the formula (4) is titanium tetrachloride.
32. A process according to any preceding claim, **characterized** in that in addition to said titanium compound having the formula (4), a titanium compound having the formula (7):



wherein each same or different R^5 is a C_1 - C_{20} alkyl, preferably a C_2 - C_8 alkyl, most preferably a C_2 - C_6 alkyl, each same or different X^3 is a halogen, preferably chlorine, n^4 is an integer 1-4, and Ti is quadrivalent titanium, is reacted.

33. A process according to claim 32, **characterized** in that titanium tetrachloride and titanium tetra C_1 - C_6 -alkoxide are reacted.

34. A process according to any of claims 2-33, **characterized** in that said second reaction product is contacted with said titanium compound having the formula (4) in a ratio moles of said titanium compound/g of the support of 0.01-10 mmol/ g of the support, preferably 0.1-2 mmol/g of the support.

35. A process according to any of claims 2-34, **characterized** in that said second reaction product is contacted with said titanium compound having the formula (4) in a ratio moles of said titanium compound/total moles of the magnesium of 0.05-2 mol/mol, preferably 0.1-1.2 mol/mol, most preferably 0.2-0.7 mol/mol.

36. A high activity catalyst component for the production of olefin polymers, **characterized** in that it has been prepared by a process according to one of claims 1-35.

37. A high activity catalyst component according to claim 36, **characterized** in that it has high activity both when producing low melt flow rate ethylene polymer and high melt flow rate polymer.

38. A polyethylene composition produced in at least two polymerization stages using a catalyst according to claim 36 or 37 and having an $SHI_{5/300}$ higher than 60, **characterized** in that it has a low gel level.

39. A film produced from a composition according to claim 38, **characterized** in that the number of gels in size class 0.3-0.7 mm and >0.7 mm are < 20 and 0 respectively.

40. A polyethylene composition produced in at least two polymerization stages using a catalyst component according to claim 36 or 37 and having an MFR₂₁ between 5 and 15 and an $SHI_{2.7/210}$ higher than 40, **characterized** in that when compounded with a carbon black additive, the resulting compound has a low dispersion value.

41. A polyethylene composition according to claim 40, **characterized** in that it has a dispersion (ISO-rating) lower than 5.

42. Use of a high activity catalyst component according to any of claims 36 or 37 in the polymerization of olefins, preferably in the polymerization of ethylene homopolymers and copolymers.

43. Use according to claim 42, together with a cocatalyst having the formula (9):



wherein R^6 is a C_1 - C_{20} alkyl, preferably a C_1 - C_{10} alkyl, most preferably a C_2 - C_6 alkyl such as ethyl, X is a halogen, preferably chlorine, n is 1 to 3, more preferably 2 or 3, most preferably 3.

(57) Abstract

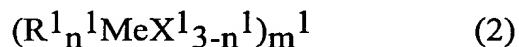
A catalyst having high activity, low hydrogen sensitivity and low gel productivity in the polymerization of ethylene has been prepared. The preparation comprises the steps of reacting:

a support comprising a magnesium halide compound having the formula (1):



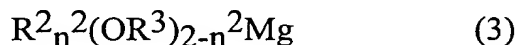
wherein each same or different R is a C₁-C₂₀ alkyl, a C₇-C₂₆ aralkyl, a C₁-C₂₀ alkoxy or a C₇-C₂₆ aralkoxy, each same or different X is a halogen, and n is an integer 1 or 2,

an alkyl metal halide compound having the formula (2):



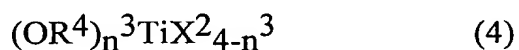
wherein Me is B or Al, each same or different R¹ is a C₁-C₁₀ alkyl, each same or different X¹ is a halogen, n¹ is an integer 1 or 2, and m¹ is an integer 1 or 2,

a magnesium composition containing magnesium bonded to a hydrocarbyl and magnesium bonded to a hydrocarbyl oxide, said magnesium composition having the empirical formula (3):



wherein each same or different R² is a C₁-C₂₀ alkyl, each same or different R³ is a C₁-C₂₀ alkyl, n² is between 0.01 and 1.99, and

a titanium halide compound having the formula (4):



wherein each same or different R⁴ is a C₁-C₂₀ alkyl, each same or different X² is a halogen, n³ is 0 or an integer 1-3, and Ti is quadrivalent titanium.

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PATENT COOPERATION TREATY

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

PCT

To:

Awapatent AB
Box 5117
200 71 MALMÖ

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1999 -11- 29

AWAPATENT, Malmö

NOTIFICATION OF RECEIPT OF DEMAND BY COMPETENT INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

(PCT Rules 59.3(e) and 61.1(b), first sentence
and Administrative Instructions, Section 601(a))

Date of mailing
(day/month/year)

26 -11- 1999

Applicant's or agent's file reference

2991406 / EW

IMPORTANT NOTIFICATION

International application No.

PCT/SE99/01195

International filing date (day/month/year)

01-07-1999

Priority date (day/month/year)

06-07-1998

Applicant

Borealis Polymers Oy
et al

1. The applicant is hereby notified that this International Preliminary Examining Authority considers the following date as the date of receipt of the demand for international preliminary examination of the international application:

26-11-1999

2. This date of receipt is:

- ☒ the actual date of receipt of the demand by this Authority (Rule 61.1(b)).
- ☐ the actual date of receipt of the demand on behalf of this Authority (Rule 59.3(e)).
- ☐ the date on which this Authority has, in response to the invitation to correct defects in the demand (Form PCT/IPEA/404), received the required corrections.

3. ☐ **ATTENTION:** That date of receipt is **AFTER** the expiration of 19 months from the priority date. Consequently, the election(s) made in the demand does (do) not have the effect of postponing the entry into the national phase until 30 months from the priority date (or later in some Offices) (Article 39(1)). Therefore, the acts for entry into the national phase must be performed within 20 months from the priority date (or later in some Offices) (Article 22). For details, see the *PCT Applicant's Guide*, Volume II.

- ☐ (If applicable) This notification confirms the information given by telephone, facsimile transmission or in person on:

4. Only where paragraph 3 applies, a copy of this notification has been sent to the International Bureau.

Name and mailing address of the IPEA/

Patent- och registreringsverket
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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference PC-2991406	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/SE99/01195	International filing date (day/month/year) 01.07.1999	Priority date (day/month/year) 06.07.1998
International Patent Classification (IPC) or national classification and IPC ₇ C 08 L 23/04		
Applicant Borealis Technology OY et al		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 3 sheets, including this cover sheet.

☐ This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of _____ sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☐ Certain observations on the international application

Date of submission of the demand 26.11.1999	Date of completion of this report 14.06.2000
Name and mailing address of the IPEA/SE Patent- och registreringsverket Box 5055 S-102 42 STOCKHOLM Facsimile No. 08-667 72 88	Authorized officer Hélène Erikson/Els Telephone No. 08-782 25 00

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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/SE99/01195

I. Basis of the report

1. This report has been drawn on the basis of *(Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.)*:

- ☒ the international application as originally filed.
- ☐ the description, pages _____, as originally filed,
 pages _____, filed with the demand,
 pages _____, filed with the letter of _____,
 pages _____, filed with the letter of _____.
- ☐ the claims, Nos. _____, as originally filed,
 Nos. _____, as amended under Article 19,
 Nos. _____, filed with the demand,
 Nos. _____, filed with the letter of _____,
 Nos. _____, filed with the letter of _____.
- ☐ the drawings, sheets/fig _____, as originally filed,
 sheets/fig _____, filed with the demand
 sheets/fig _____, filed with the letter of _____,
 sheets/fig _____, filed with the letter of _____.

2. The amendments have resulted in the cancellation of:

- ☐ the description, pages _____
- ☐ the claims, Nos. _____
- ☐ the drawings, sheets/fig _____

3. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the supplemental Box (Rule 70.2(c)).

4. Additional observations, if necessary:

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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/SE99/01195

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**1. Statement**

Novelty (N)	Claims	<u>1-15</u>	YES
	Claims		NO
Inventive step (IS)	Claims	<u>1-15</u>	YES
	Claims		NO
Industrial applicability (IA)	Claims	<u>1-15</u>	YES
	Claims		NO

2. Citations and explanations

The claimed invention relates to a multimodal polyethylene composition for pipes. Said multimodal polyethylene comprises a low molecular weight ethylene homopolymer fraction and a high molecular weight ethylene copolymer fraction. Also a pressure pipe comprising the multimodal polymer composition is claimed.

US 5 494 965 A1 relates to a process for producing bimodal olefin polymers of a special type, viz. a mechanical combination of a unimodal low molecular weight ethylene polymer and a bimodal ethylene polymer. The composition may be used for a plurality of different fields of applications and therefore it has a wide spectrum of features. This is in contrast to the claimed invention which specifically relates to a composition for pipes, which requires a special combination of features e.g. good processability, high rapid crack propagation resistance, high slow crack growth resistance and high strength. The specific pipe requirements of the claimed invention are not disclosed in US 5 494 965.

In view of the above, the cited document only discloses the general state of the art, which is not considered to be of particular relevance. Therefore, the claimed invention is ~~considered to fulfil the requirements of novelty, inventive step and industrial applicability.~~

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PATENT COOPERATION TREATY

PCT

From the INTERNATIONAL BUREAU

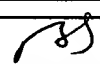
NOTIFICATION OF THE RECORDING
OF A CHANGE(PCT Rule 92bis.1 and
Administrative Instructions, Section 422)

To:

AWAPATENT AB
P.O. Box 5117
S-200 71 Malmö
SUÈDE

Date of mailing (day/month/year) 26 June 2000 (26.06.00)	IMPORTANT NOTIFICATION
Applicant's or agent's file reference 2991406	
International application No. PCT/SE99/01195	International filing date (day/month/year) 01 July 1999 (01.07.99)

1. The following indications appeared on record concerning:		
<input checked="" type="checkbox"/> the applicant	<input type="checkbox"/> the inventor	<input type="checkbox"/> the agent <input type="checkbox"/> the common representative
Name and Address BOREALIS POLYMERS OY P.O. Box 330 FIN-06101 Porvoo Finland	State of Nationality FI	State of Residence FI
	Telephone No.	
	Facsimile No.	
	Teleprinter No.	
2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:		
<input checked="" type="checkbox"/> the person	<input checked="" type="checkbox"/> the name	<input type="checkbox"/> the address <input type="checkbox"/> the nationality <input type="checkbox"/> the residence
Name and Address BOREALIS TECHNOLOGY OY P.O. Box 330 FIN-06101 Porvoo Finland	State of Nationality FI	State of Residence FI
	Telephone No.	
	Facsimile No.	
	Teleprinter No.	
3. Further observations, if necessary:		
4. A copy of this notification has been sent to:		
<input checked="" type="checkbox"/> the receiving Office	<input type="checkbox"/> the designated Offices concerned	
<input type="checkbox"/> the International Searching Authority	<input checked="" type="checkbox"/> the elected Offices concerned	
<input checked="" type="checkbox"/> the International Preliminary Examining Authority	<input type="checkbox"/> other:	

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland	Authorized officer  Beate Giffo-Schmitt
Facsimile No.: (41-22) 740.14.35	Telephone No.: (41-22) 338.83.38

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PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

16
REC'D 04 AUG 2000

WIPO

PCT

Applicant's or agent's file reference PC-2991406	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/SE99/01195	International filing date (day/month/year) 01.07.1999	Priority date (day/month/year) 06.07.1998
International Patent Classification (IPC) or national classification and IPC ₇ C 08 L 23/04		
Applicant Borealis Technology OY et al		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 3 sheets, including this cover sheet.

☐ This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of _____ sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☐ Certain observations on the international application

Date of submission of the demand 26.11.1999	Date of completion of this report 14.06.2000
Name and mailing address of the IPEA/SE Patent- och registreringsverket Box 5055 S-102 42 STOCKHOLM Facsimile No. 08-667 72 88	Authorized officer Hélène Erikson/Els Telephone No. 08-782 25 00

Form PCT/IPEA/409 (cover sheet) (January 1999)

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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/SE99/01195

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International application No.

PCT/SE99/01195

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